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(54) A method for stabilising a fluosilicic acid solution

(57) A method for stabilising a fluosilicic acid solution containing a trace of sulphate during storing and transportation in a stainless steel container, the method comprises adding food grade oxidising agent, eg hydrogen peroxide, to the solution to the amount of 0.02% to 0.07% by weight of the solution. In the example described, the solution contains 85% water, 14% fluosilicic acid and approximately 0.2% sulphate.

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A METHOD FOR STABILISING A FLUOSILICIC ACID SOLUTION

The present invention relates to a method for stabilising a fluosilicic acid solution containing a trace of sulphate during storing in a metal container, and in particular, during storage in a stainless steel container. The invention also relates to a stabilised fluosilicic acid solution as well as a container containing the stabilised fluosilicic acid solution.

Fluosilicic acid is used as a source of fluoride in the fluoridation of local authority water supply schemes for human consumption. In general, the fluosilicic acid is added to the water supply in relatively low proportions as the water is being metered from a reservoir. The fluosilicic acid is normally supplied in a water solution containing approximately 14% by weight of fluosilicic acid and is normally transported to the site in a stainless steel container and may be stored on site in a stainless steel container. In general, fluosilicic acid contains trace impurities, one of which is a sulphate. When stored in a metal container, in particular, a stainless steel container, the fluosilicic acid reacts with the metal of the stainless steel container in a reducing reaction, which reduces the sulphate in the fluosilicic acid to sulphide and hydrogen sulphide is formed. This results in a unpleasant "rotten egg" type odour. While the reduction of the sulphate to

sulphide does not affect the fluosilicic acid solution, it is nonetheless objectionable.

There is therefore a need for a method for stabilising a fluosilicic acid solution containing a trace of sulphate during storing and/or transportation in a metal container. There is also a need for a stabilised fluosilicic acid solution and a metal container containing the stabilised fluosilicic acid solution.

The present invention is directed towards providing such a method, a stabilised fluosilicic acid solution and a metal container containing the fluosilicic acid solution.

According to the invention, there is provided a method for stabilising a fluosilicic acid solution containing a trace of sulphate when stored in a metal container, the solution comprising up to 30% by weight of fluosilicic acid and up to 1% by weight of sulphate, the method comprising the step of adding a food grade oxidising agent to the solution, the oxidising agent constituting in the range of 0.02% to 0.07% by weight of the solution.

In one embodiment of the invention the oxidising agent constitutes in the range of 0.03% by weight to 0.05% by weight of the solution. Preferably, the oxidising agent constitutes approximately 0.04% by weight of the solution.

In another embodiment of the invention the oxidising agent is hydrogen peroxide.

In a further embodiment of the invention the fluosilicic acid solution is stored in a stainless steel container.

In one aspect of the invention the fluosilicic acid constitutes up to 20% by weight of the solution.

In another aspect of the invention the fluosilicic acid constitutes up to approximately 14% by weight of the solution.

In another aspect of the invention the sulphate constitutes up to 0.5% by weight of the solution. In a further aspect of the invention the sulphate constitutes up to approximately 0.2% by weight of the solution.

In a still further embodiment of the invention the solution is a fluosilicic acid/water solution.

Additionally, the invention provides a stabilised fluosilicic acid solution comprising up to 30% by weight of fluosilicic acid and up to 1% by weight of sulphate and a food grade oxidising agent, the food grade oxidising agent constituting in the range of 0.02% to 0.07% by weight of the solution.

In one embodiment of the invention the oxidising agent constitutes in the range of 0.03% by weight to 0.05% by weight of the solution. Preferably, the oxidising agent constitutes approximately 0.04% by weight of the solution.

In another embodiment of the invention the oxidising agent is hydrogen peroxide.

In one aspect of the invention the fluosilicic acid solution is stored in a stainless steel container.

In another aspect of the invention the fluosilicic acid constitutes up to 20% by weight of the solution.

In a still further aspect of the invention the fluosilicic acid constitutes up to approximately 14%

by weight of the solution.

In another aspect of the invention the sulphate constitutes up to 0.5% by weight of the solution.

In another aspect of the invention the sulphate constitutes up to approximately 0.2% by weight of the solution.

In a still further aspect of the invention the solution is a fluosilicic acid/water solution.

Further the invention a metal container containing the stabilised solution of fluosilicic acid according to the invention.

In one embodiment of the invention the metal container is of stainless steel.

The invention will be more clearly understood from the following description of a preferred embodiment thereof, given by way of the following non-limiting example.

A fluosilicic acid solution comprises the following constituents in the proportions by weight of the solution set out below:

water	85 %
fluosilicic acid	14 %
sulphate	0.2%
other impurities	0.8%

The fluosilicic acid solution is for use in the fluoridization of a local authority water supply scheme for human consumption. The fluosilicic acid is to be transported by road in a tanker having a stainless steel tank within which the fluosilicic acid is to be transported. The fluosilicic acid may also be stored prior to transportation and on the local authority water supply site in a stainless steel container. The fluosilicic acid solution is stabilised to prevent the sulphate being reduced as a result of reacting with the stainless steel container. Stabilisation is achieved by adding a food grade oxidising agent to the fluosilicic acid solution. In this embodiment of the invention, the oxidising agent is food grade hydrogen peroxide and constitutes approximately 0.04% by weight of the fluosilicic acid solution. The hydrogen peroxide may be added to the solution prior to being delivered into the stainless steel container, simultaneously as the fluosilicic acid solution is being delivered into the container, or just as the fluosilicic acid solution has been delivered into the container.

It has been found that the presence of the hydrogen peroxide in the fluosilicic acid solution prevents reduction of the sulphate in the fluosilicic acid solution forming hydrogen sulphide. The above described fluosilicic acid solution stabilised with hydrogen peroxide failed to exhibit any trace of hydrogen sulphide after being stored in a stainless steel tank for five days.

Why these new and surprising results are achieved are not fully understood, however, the following is advanced by way of explanation. It has been found that solutions of fluosilicic acid when stored in stainless steel containers produce blackening of the stainless steel in the containers, along with the production of a greenish-black colour of the fluosilicic acid solution, and the evolution of hydrogen sulphide. It is believed that the blackening of the stainless steel is caused by the fluosilicic acid attacking the stainless steel in a reducing reaction. In the process of the reducing reaction, sulphate present as an impurity in the fluosilicic acid is reduced to sulphide. The sulphide reacts with the iron in the stainless steel to form a black insoluble ferrous sulphide layer. It is believed that the greenish-black colour of the fluosilicic acid solution arises from solubilisation of non-ferrous

metals in the stainless steel.

Tests have been carried out on metal coupons of various stainless steels, namely, stainless steel 304, stainless steel 316 and stainless steel 316L, which have been immersed in respective beakers of fluosilicic acid solutions. In the tests it has been demonstrated that the coupons immersed in the fluosilicic acid solutions develop a black coating after a period of two to six hours in the solutions, and additionally, the fluosilicic acid solution turns green. On agitation of the beaker, specks of the black coating dispersed in the fluosilicic acid solution give a greenish-black appearance to the fluosilicic acid solution. The solution also emits a strong smell of hydrogen sulphide. When similar tests were carried out with stainless steel coupons with similar grades of stainless steel immersed in fluosilicic acid solutions stabilised with food grade hydrogen peroxide, wherein the food grade hydrogen peroxide constituted in the range of 0.02% to 0.07% of the solution, no blackening of the stainless steel coupons occurred. In fact, the surfaces of the stainless steel coupons remained shining and bright. Additionally, the stabilised fluosilicic acid solution remained colourless and there was no smell of hydrogen sulphide, indicating the absence of hydrogen sulphide

in the solution. The stainless steel coupons were left in the respective fluosilicic acid solutions for ten days, and after ten days, no blackening of the stainless steel coupons was detected, the colour of the fluosilicic acid solution remained unchanged, and there was no indication of the presence of hydrogen sulphide.

While the food grade oxidising agent has been described as being food grade hydrogen peroxide, it is envisaged that other suitable food grade oxidising agents may be used.

CLAIMS

1. A method for stabilising a fluosilicic acid solution containing a trace of sulphate when stored in a metal container, the solution comprising up to 30% by weight of fluosilicic acid and up to 1% by weight of sulphate, the method comprising the step of adding a food grade oxidising agent to the solution, the oxidising agent constituting in the range of 0.02% to 0.07% by weight of the solution.

2. A method as claimed in Claim 1 in which the oxidising agent constitutes in the range of 0.03% by weight to 0.05% by weight of the solution.

3. A method as claimed in Claim 2 in which the oxidising agent constitutes approximately 0.04% by weight of the solution.

4. A method as claimed in any preceding claim in which the oxidising agent is hydrogen peroxide.

5. A method as claimed in any preceding claim in which the fluosilicic acid solution is stored in a stainless steel container.

6. A method as claimed in any preceding claim in which the fluosilicic acid constitutes up to 20% by

weight of the solution.

7. A method as claimed in any preceding claim in which the fluosilicic acid constitutes up to approximately 14% by weight of the solution.

8. A method as claimed in any preceding claim in which the sulphate constitutes up to 0.5% by weight of the solution.

9. A method as claimed in any preceding claim in which the sulphate constitutes up to approximately 0.2% by weight of the solution.

10. A method as claimed in any preceding claim in which the solution is a fluosilicic acid/water solution.

11. A method for stabilising a fluosilicic acid solution containing a trace of sulphate when stored in a metal container, the method being substantially as described herein with reference to the example.

12. A stabilised fluosilicic acid solution comprising up to 30% by weight of fluosilicic acid and up to 1% by weight of sulphate and a food grade oxidising agent, the food grade oxidising agent constituting in

the range of 0.02% to 0.07% by weight of the solution.

13. A stabilised fluosilicic acid solution as claimed in Claim 12 in which the oxidising agent constitutes in the range of 0.03% by weight to 0.05% by weight of the solution.

14. A stabilised fluosilicic acid solution as claimed in Claim 13 in which the oxidising agent constitutes approximately 0.04% by weight of the solution.

15. A stabilised fluosilicic acid solution as claimed in any of Claims 12 to 14 in which the oxidising agent is hydrogen peroxide.

16. A stabilised fluosilicic acid solution as claimed in any of Claims 12 to 15 in which the fluosilicic acid solution is stored in a stainless steel container.

17. A stabilised fluosilicic acid solution as claimed in any of Claims 12 to 16 in which the fluosilicic acid constitutes up to 20% by weight of the solution.

18. A stabilised fluosilicic acid solution as claimed in any of Claims 12 to 17 in which the fluosilicic acid constitutes up to approximately 14% by weight of

the solution.

19. A stabilised fluosilicic acid solution as claimed in any of Claims 12 to 18 in which the sulphate constitutes up to 0.5% by weight of the solution.

20. A stabilised fluosilicic acid solution as claimed in any of Claims 12 to 19 in which the sulphate constitutes up to approximately 0.2% by weight of the solution.

21. A stabilised fluosilicic acid solution as claimed in any of Claims 12 to 20 in which the solution is a fluosilicic acid/water solution.

22. A stabilised fluosilicic acid solution substantially as described herein with reference to the example.

23. A metal container containing the stabilised solution of fluosilicic acid of any of Claims 12 to 22.

24. A metal container as claimed in Claim 23 in which the metal container is of stainless steel.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition L) C1A (ABIX)

(ii) Int Cl (Edition 5) C01B

Search Examiner
C A CLARKE

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI; CLAIMS; JAPIO

Date of Search
26 MARCH 1993

Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1309086 - (FISONS)	1,4,10 AND 15 AT LEAST

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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